Review

Review on the electrochemical processes for the treatment of sanitary landfill leachates: Present and future

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ABSTRACT

Due to its properties and composition, sanitary landfill leachate is one of the major environmental problems concerning water pollution. The optimization of the leachate treatment, in order to fully reduce the negative impact on the environment, is a nowadays challenge. Advanced technologies for the treatment of sanitary landfill leachates have received increasing attention over the past decade. This paper presents a general review of efficient electrochemical technologies developed to decontaminate sanitary landfill leachates. An overview of the fundamental aspects of electrochemical methods, such as electro-coagulation, electro-Fenton and electrochemical oxidation, is provided and updated information on the application of these technologies to sanitary landfill leachates is given. The effect of the main process variables of these electrochemical technologies in the sanitary landfill leachates treatment effectiveness is discussed and a critical analysis of the prime benefits and drawbacks of its application is made.

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Contents

1. Introduction

Population growth and new patterns of consumption have been leading to the production of huge amounts of municipal solid wastes that are usually discarded in sanitary landfills, since this is a relatively simple procedure with low cost [1]. However, as a result of the rainwater percolation through the wastes, extracting and bringing with it several pollutant materials, a very complex wastewater is produced, usually known as sanitary landfill leachate. Several types of pollutants can be found in the sanitary landfill leachates composition, such as all types of organic

and inorganic compounds, some of them refractory and toxic, and heavy metals [1,2]. Due to its complex, recalcitrant and varied composition, sanitary landfill leachates represent a significant source of pollution, presenting an accumulative, threatening and detrimental effect to the survival of aquatic life forms and ecological balances [3]. An inadequate leachate management involves serious risks, particularly the contamination of water resources, at the surface and groundwater, and soils, and consequently, it may induce genome damage in the population that consumes the contaminated water [1–4].

Biological reactors, with nitrification/denitrification steps, followed by membrane technologies, are commonly used to treat sanitary landfill leachates. However, due to the variability in the quality and quantity of the leachate throughout the life span of the treatment plant, these conventional treatments may become ineffective. Thus, it is very important to apply reliable and

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effective treatment technologies, capable of deal with such complex effluents.

Electrochemical treatments have been showing high effectiveness in the elimination of persistent pollutants and several studies have described the application of these methods in the treatment of complex effluents [5–10]. In fact, electrochemical technologies provide several advantages, being the inherent advantage the environmental compatibility, since the main species involved in the oxidation process are electrons and oxidant agents produced in situ. Other advantages include the use of simple equipment, easy operation, robustness, versatility and amenability to automation [11,12]. Among the electrochemical technologies, the most studied for the treatment of sanitary landfill leachate are electrocoagulation (EC), electro-Fenton (EF) and electrochemical oxidation (EO). There are several reports describing the application of these technologies to leachates, as a single treatment, or combined with other methods. Photoassisted systems, like photoelectro-Fenton and photoelectrocatalysis, have also received great attention in the last years, but will not be discussed in this paper, since they are outside the scope of this review.

The aim of this paper is to present a general review of the most relevant applications of the electrochemical methods in the treatment of sanitary landfill leachates, to point out some scarcely studied aspects, whose development may contribute to the application of these technologies at an industrial scale, and to present the future perspectives for the application of the electrochemical processes in the treatment of effluents with high organic load. Fundamentals of EC, EF and EO technologies are briefly presented to better understand their advantages and limitations in the treatment of the sanitary landfill leachates.

2. Sanitary landfill leachate characteristics and environmental impacts

The composition of sanitary landfill leachates varies depending on landfills characteristics, such as: [13,14] the waste type received at the disposal site and its decomposition degree; the climatic variation during the waste disposal; the filling process regarding waste compaction, landfill cover and height of landfill layers; and the landfill environment – waste degradation phase, humidity, precipitation, temperature, etc. These aspects are interconnected and their combination contributes to the overall variance in the leachate quality and composition.

According to the age, the sanitary landfill can be classified as young (less than 5 years), medium age (5–10 years) and old (more than 10 years) [3]. As the landfill age increases, leachates parameters, such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), BOD/COD ratio and pH vary considerably [3]. Fig. 1 represents the trend in the variation of the main parameters that characterize sanitary landfill leachates with the age of the sanitary landfill [3,7,13,15,16]. It can be seen that COD and BOD concentrations decrease as time proceeds and the leachate organic waste degradation goes through the successive aerobic, acetogenic, methanogenic and stabilization stages [13]. In fact, most of the biodegradable organic matter, which can be evaluated by BOD value, is decomposed in the stabilization process and therefore BOD/COD ratio decreases with time, because the non-biodegradable organic matter that contributes to the portion of COD will largely stay unchanged in this process [17]. On the contrary, pH increases with age [7]. In sum, leachates from young sanitary landfills are characterized by high COD concentrations (>10,000 mg L^{-1}) and BOD/COD ratios (0.5–1), whereas in old landfills leachates present COD concentrations below 4000 mg L^{-1} and BOD/COD ratios below 0.1 [3]. Besides the variation of the landfill leachates composition with the landfill age, it also varies from place to place, leading to huge fluctuations in the values of the most representative characterization parameters (Fig. 1). Apart from the represented parameters in Fig. 1, there are more than 200 compounds that have already been identified in sanitary landfill leachates, such as aromatic and halogenated compounds, phenols, pesticides and several heavy metals [1,2,14].

In addition to the organic load, ammonia nitrogen (AN) is of great environmental concern in landfill leachates [7]. It is released from the wastes, mainly by decomposition of proteins, and it has been found in leachates at concentrations ranged from 0.2 to 13,000 mg L^{-1} [13]. Ammonia nitrogen concentration does not have an obvious decreasing trend with time, except due to dilution effects, and may disrupt biological units for leachate treatment due to its toxicity. Therefore, AN has been identified as the most significant component in the leachate in a long term [15].

3. Electrochemical technologies for the treatment of sanitary landfill leachates

The electrochemical technologies are based on electron transfer between electrodes and the electrolytic solution, by applying an electric field between anode and cathode, made of specific materials, appropriate for each electrochemical technology. The applied current/potential difference provides the driving force necessary to promote the oxidation/reduction reactions of the solution' pollutants, contained in the electrochemical cell. The environmental compatibility, versatility and amenability of automation of these technologies [12], as well as the high effectiveness shown in the elimination of persistent pollutants [5–10], led to an increased number of experimental works.

In the subsections below, the fundamentals of electrocoagulation, electro-Fenton and electrochemical oxidation and the main results obtained from their application to sanitary landfill leachates treatment are presented.

3.1. Electrocoagulation

Electrocoagulation is a process that uses consumable electrodes to supply ions to the solution/suspension, allowing suspended, emulsified, or dissolved contaminants to form agglomerates. The coagulating ions are produced in situ and three different stages can be identified: [18] (i) formation of the coagulants by electrolytic oxidation of the "sacrificial electrode", (ii) destabilization
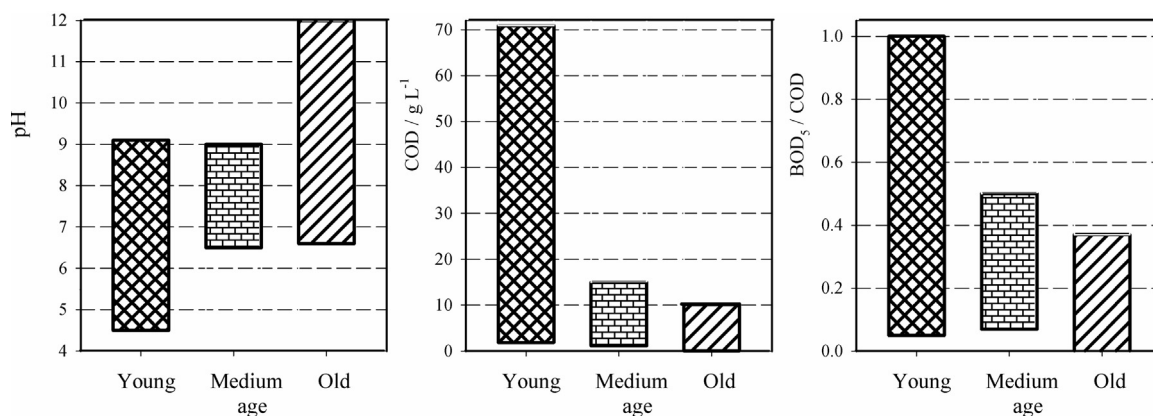
Fig. 1. pH, COD and BOD_5/COD typical values for leachates from young, medium age and old landfills.

of the contaminants and particulate suspension and breaking of emulsions and (iii) aggregation of the destabilized phases to form flocs. The contaminants present in the solution are treated either by chemical reactions and precipitation or by physical and chemical attachment to colloidal materials generated by the electrode corrosion [19]. The coagulated particles can be separated from the liquid phase by sedimentation or by electroflotation, when they are attached to H_2 bubbles, evolved at the cathode, and transported to the top of the solution [5,19]. The basic EC process is schematically presented in Fig. 2.

Iron and aluminum are the most widely used EC electrode materials, since they are cheap, readily available and effective [20]. When iron is the anode in the EC process, Fe^{2+} is dissolved into the solution from Fe oxidation at the anode and produce iron hydroxide, Fe $(OH)_n$, where $n = 2$ or 3. The $Fe(OH)_2$ and $Fe(OH)_3$ flocs formed have strong affinity for colloids, dispersed particles and ionic species and cause the flocculation, which generates bigger particles. Fe^{3+} ions may also be present and, depending on the pH, different insoluble hydroxide mononuclear complexes may be formed [21]. In the case of EC with Al, the electrolytic dissolution of the aluminum anode produces species, such as Al^{3+} and $Al(OH)_2^+$ that are transformed initially into $Al(OH)_3$ and finally polymerized to $Al_n(OH)_{3n}$ [21]. However, depending on the pH of the aqueous medium, other ionic species, such as $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$ and $Al(OH)_4^-$ may also be present in the system.
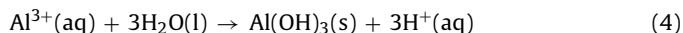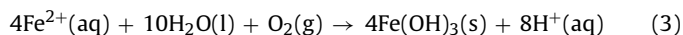
Two different mechanisms have been described for the production of the metal hydroxide, depending on the pH of the solution [22]. The reactions for iron or aluminum anodes are given in Eqs. (1)–(8).
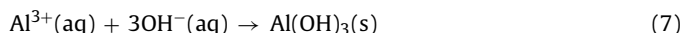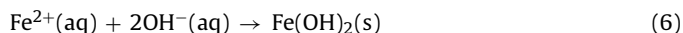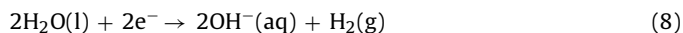
• Mechanism 1 (acidic medium)

Anode:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \qquad (1)$$

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^- \qquad (2)$$

In solution:

$$4Fe^{2+}(aq) + 10H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(s) + 8H^+(aq) \qquad (3)$$

$$Al^{3+}(aq) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3H^+(aq) \qquad (4)$$

Cathode:

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad (5)$$

• Mechanism 2 (alkaline medium)

Anode: Eqs. (1) and (2)
  In solution:

$$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s) \qquad (6)$$

$$Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s) \qquad (7)$$

Cathode:

$$2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g) \qquad (8)$$

EC has been successfully applied in the treatment of sanitary landfill leachates and there are several papers describing those studies [20,22–31]. The conditions used in the experiments as well as the main results obtained are summarized in Table 1. Several process variables can influence the EC treatment efficiency, such as reactor design, electrode material, current density, pH, conductivity, etc. The main goal in the design of an EC cell is to achieve the maximum efficiency of the process.

In its simplest form, an electrocoagulating reactor may be made up of an electrolytic cell with one anode and one cathode. When connected to an external power source, the anode material will electrochemically corrode due to oxidation, while the cathode will be subjected to passivation. However, this arrangement may not be suitable for wastewater treatment, since for a workable rate of metal dissolution, the use of electrodes with large surface area is required [9,19].
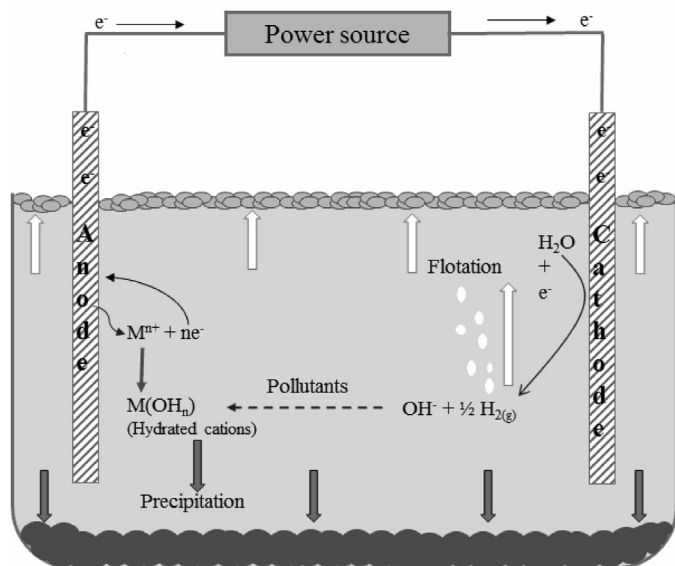

Fig. 2. Schematic diagram of a two-electrode batch EC cell.
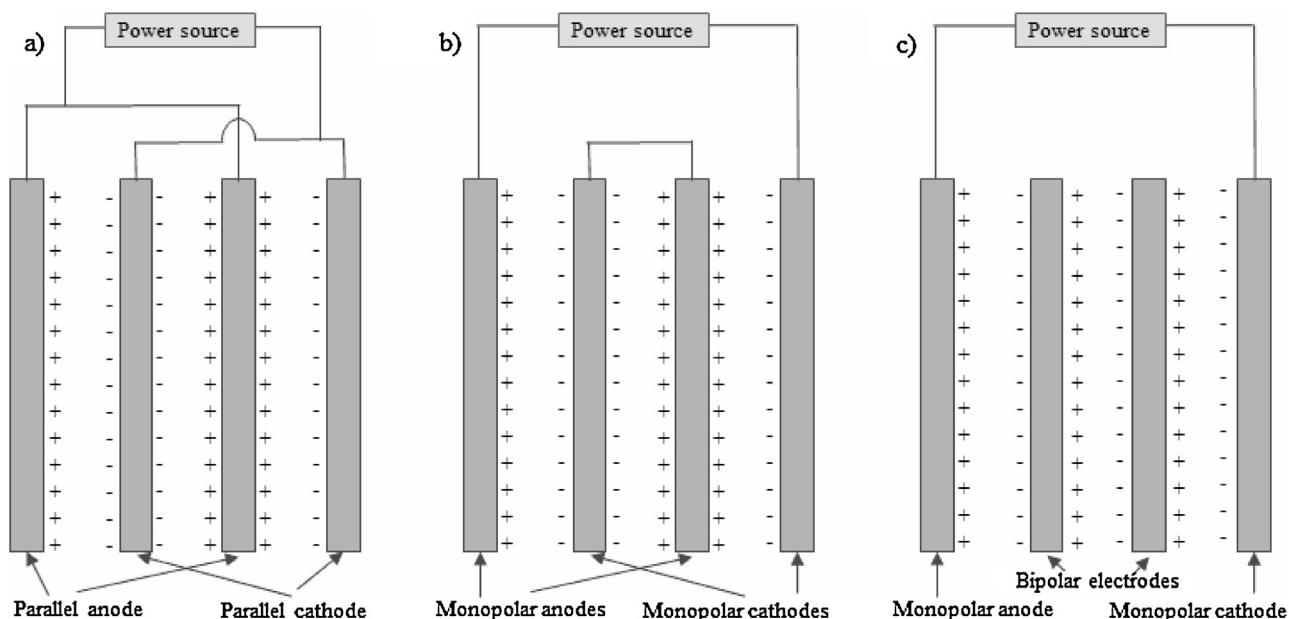Source: adapted from [18].

Table 1
A summary of research results previously reported for the degradation of sanitary landfill leachates by electrocoagulation.

Reactor design	Electrode material	Inter-electrode gap/cm	Current density/A m^{-2}	Electrolysis time/min	Stirring speed/rpm	pH$_0$	COD$_0$/mg L^{-1}	AN$_0$/mg L^{-1}	COD removal/%	AN removal/%	Energy consumption	References
Batch reactor with 2 electrodes in parallel connection	Al	6.5	348	30	No	8.2	12860	2240	45	9	12.5 kW h m^{-3} or 0.46 W h (g COD)$^{-1}$	[22]
			631		200				44	16	NS	
					No				59	14	39.7 kW h m^{-3} or 1.1 W h (g COD)$^{-1}$	
	Fe				No				35	11	NS	
Batch reactor with 14 electrodes in parallel connection	Al	0.3	NS	NS	NS	7.7	4022	NS	88	NS	NS	[31]
	Fe								90			
Continuous reactor with 2 bipolar electrodes	Al	0.2–1	NS	NA	No	7.2	380	NS	45	NS	NS	[25]
Batch reactor with 6 electrodes in parallel connection	Fe	0.9	50	120	200	6.5	11000	1247	30[a]	NS	1.0 W h (g COD)$^{-1}$	[28]
			200			3			41		3.5 W h (g COD)$^{-1}$	
						6.5			53		6.3 W h (g COD)$^{-1}$ [a]	
						8			47[a]		6.9 W h (g COD)$^{-1}$	
			300			6.5			57[a]		8.7 W h (g COD)$^{-1}$	
Batch reactor with 2 electrodes in parallel connection	Al	0.5	250	30	150	7.6–8.9	31200[a]	NS	60[a]	NS	NS	[24]
		2.8	125						56			
			250						70[a]			
					50				58[a]			
			500		150				70		22 kW h m^{-3}	
	Fe								68		19.6 kW h m^{-3}	
Batch reactor with 10 electrodes in parallel connection	Al	1	30	30	200	6.7	2566	386	21	21	NS	[20]
	Fe		20			6.7			24	20		
			30			3.9			27	14		
						6.7			33	25		
						10			22	16		
			50			6.7			93	32		
Batch reactor with 4 electrodes in parallel connection	Al	1.6	79	30	No	6.6–7.0	6200	110	29	NS	NS	[30]
			198						45			
Batch reactor with 2 electrodes in parallel connection	Fe	2.3	200[a]	40	No	4.0	12650	NS	56	NS	7.4 kW h m^{-3}	[26,27]
				20		8.6			19		3.2 kW h m^{-3}	
				30	600	8.6			19		4.3 kW h m^{-3}	
			350[a]	10	No	8.6			17		4.6 kW h m^{-3}	
			300[a]	20		4.0	3200		39		6.2 kW h m^{-3}	
				10		7.4			5		4.3 kW h m^{-3}	
				20	600	7.4			27		6.7 kW h m^{-3}	
			400[a]	10	No	7.4			18		5.1 kW h m^{-3}	
Batch reactor with 2 electrodes in parallel connection	Fe	1	625[a]	180	No	6	21700	1200	42[a]	1[a]	NS	[23]
						8.5			40[a]	8[a]		
Batch reactor with 2 electrodes in parallel connection	Al	2	23	210	Yes	8	260	187	33[a]	NS	18 W h (g COD)$^{-1}$	[29]
			95						56[a]	0	135 W h (g COD)$^{-1}$	
		4	23						33[a]	NS	70 W h (g COD)$^{-1}$	
			95						56[a]	NS	165 W h (g COD)$^{-1}$	

NA–Not applied; NS–Not specified.

[a] Value obtained indirectly from data presented in the paper or from a figure.

Fig. 3. Different electrodes' arrangement within the electrochemical cell: (a) monopolar electrodes in parallel connections; (b) monopolar electrodes in series connections and (c) dipolar electrodes in series connections.
Source: adapted from [32].

EC reactors can present different electrodes' arrangement within the electrochemical cell, namely, monopolar electrodes in parallel connections and monopolar and dipolar electrodes in series connections (Fig. 3). Inside the EC reactor, the electrodes number can vary by inserting/removing electrodes between those at the cell ends. In parallel connections arrangement (Fig. 3a), the electric current is divided between all the electrodes, being the potential difference the required by a single cell. In the series arrangement, equal current intensity flows through all the electrodes and, although a higher potential difference is required, it has proved to be more economical [32]. The use of bipolar electrodes in the series connections cells (Fig. 3c) presents the advantage of eliminating the interconnections between the inner electrodes, since only two monopolar electrodes are connected to the electric power source, giving a simple physical set-up which facilitates maintenance under practical applications [32].

As it can be seen in Table 1, for most of the EC experiments performed with sanitary landfill leachates, a batch reactor with monopolar electrodes in parallel connection has been used, varying the number of electrodes between 2 and 14.

There are several studies reporting the effect of the electrode material, iron or aluminum, on the EC treatment efficacy of sanitary landfill leachates (Table 1). High treatment efficacies were obtained with both electrode materials, depending on the leachate characteristics and operating variables imposed. COD removals up to 21,000 $mg L^{-1}$ after 30 min of electrolysis at 500 $A m^{-2}$ were reported for both electrode materials, when applied to 0.5 L of a leachate with an initial BOD_5/COD ratio of 0.12 [24]. It is known that, despite the high coagulation efficacy of Al^{3+}, the aluminum electrodes passivation is detrimental to the reactor performance [19]. In fact, the formation of an inhibiting layer, usually an oxide on the electrode surface, will prevent metal dissolution and electron transfer, thereby limiting coagulant addition to the solution. Over time, the thickness of this layer increases, reducing the efficacy of the electrocoagulation process [19]. The presence of some anions in aqueous solution can slow down the electrode passivation, especially the presence of Cl^- that is known to largely inhibit the passivation process [19]. The adverse effect of anions, such as

HCO_3^- and SO_4^{2-} that lead to the precipitation of Ca^{2+} and Mg^{2+}, forming an insulating layer on the surface of the electrodes, can significantly be reduced if chloride ions are present [5].

According to Table 1, the more pronounced difference between the treatment efficiencies using Al or Fe electrodes was obtained in a comparative study in which the initial Cl^- concentration in the leachate was 3.1 $g L^{-1}$, being the highest efficiencies assigned to Al electrodes [22]. Also, from data presented in Table 1, and focusing on the comparative studies of both electrode materials [20,22,24,31], it can be seen that Al electrodes lead to better results than Fe electrodes in experiments where high current density values are applied. This can be consistent with the possible chemical attack on the aluminum cathode by hydroxyl ions generated during water reduction, which generates an extra amount of aluminum ions [25]. High current density promotes the formation of higher concentration of hydroxyl ions because water electrolysis at the cathode depends on the quantity of electricity which passes through the solution.

An electrical energy consumption analysis was performed by Bouhezila et al. [24] and it was found that, despite the better removal rates obtained by Al electrodes, Fe electrodes were energetically more efficient than aluminum. Also, iron is less toxic and more acceptable to be released in agriculture fields and thus can be considered as the most appropriate electrode material for the treatment of leachates by electrocoagulation processes [24].

In order to investigate the effect of inter-electrodes distance on the efficiency of the EC process in sanitary landfill leachate treatment, studies were performed where the inter-electrode distance was varied (Table 1). Bouhezila et al. [24] reported that, when the inter-electrode distance was increased from 0.5 to 2.8 cm, the removal of COD increased by about 10% after 15 min of treatment. However, for turbidity and color removal, no discernible differences were observed. Ricordel and Djelal [29] found that the differences in COD removals were not significant between 2 and 4 cm gaps. Although the obtained results of these two studies did not converge, they may be consistent since in the study performed by Bouhezila et al. [24] the organic load of the leachate and the applied current densities were significantly higher than those used

in Ricordel and Djelal [29] experiments, being the leachate volume used in this latter study much higher (4 L). Indeed, despite shorter inter-electrodes distances minimize the IR-drop between the electrodes, they also potentiate faster electrode passivation, which happens more intensely when the organic load of the leachate is high. Other EC studies performed with sanitary landfill leachates, and reported in Table 1, used inter-electrodes distances between 0.2 and 6.5 cm. Although it is a wide range, no trend is found in the influence of the inter-electrode distance on the efficacy of the EC process in sanitary landfill leachate treatment. An adequate inter-electrode distance is function of leachate characteristics and must be determined balancing the IR-drop and the passivation effects.

The effect of mechanical stirring on the EC efficacy treatment of leachates has also been studied. Ilhan et al. [22] experiments, performed with 0.5 L of leachate, using an electrode area of 45 cm^2, showed that the mixing process negatively affected the COD removal efficiency, although it increased the AN removal, according to these authors because ammonia is easily stripped by mixing. Different results were obtained by Bouhezila et al. [24], which reported an increase in COD removal and in sludge production when the magnetic stirring speed was increased from 50 rpm to 150 rpm. Norma and co-workers [26,27] studies, showed that the use of stirring increases the time needed to start, with a visible rate, the precipitation of the flocs formed in EC and consequently the iron and energy consumptions. In fact, EC process is performed by the mobilization of ions by means of applied electrical charge, and mixing operation will influence the movement of the ions in the suspension. Considering this, mixing can promote a more homogeneous solution medium that will be much more efficient for the contact between the contaminant and coagulants. On the other hand, mixing can also cause a disturbance of ions mobilization and the breakup of flocs. Depending on the experimental conditions applied, moderate stirring can be considered an advantage in EC treatment of leachates, despite the disadvantages associated to extra costs that it implies.

A key factor in the EC process is the operating current density, since it exerts a significant influence on the reaction kinetics and energy consumption. Increasing the current density, the extent of anodic dissolution of consumable electrodes increases, resulting in an increase in hydroxide flocs that promote pollutants removal. Moreover, with the increasing in current density the rate of bubble-generation increases and the bubble size decreases, resulting in a faster removal of pollutants by H$_2$ flotation [28]. There are several studies reporting the effect of current density on the EC treatment efficacy of leachates [20,22,24,26–30]. Despite the difference in leachate characteristics and in operational conditions applied in the different studies, all have shown that pollutants removal increased with the increase in current density, as can be seen in Table 1. According to the explanation given above, no other result was expected. However, when energy consumption is analyzed, the results obtained with the high current densities do not seem so appealing, since the energy consumption is greatly increased by the increase in current density. So, an optimum current density must invariably involve a trade-off between energy consumptions and efficient use of the introduced coagulant [19]. For instance, Orkun and Kuleyin [28] have found that the maximum removal rate occurred for the highest current density tested (30 mA cm^{-2}) but, when considering the energy and electrode consumptions, the optimum current density was determined as 20 mA cm^{-2}.
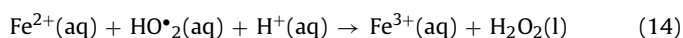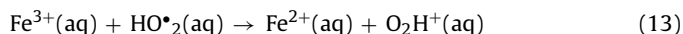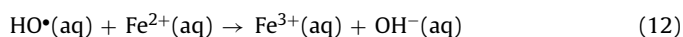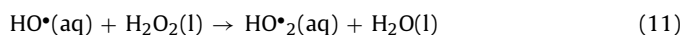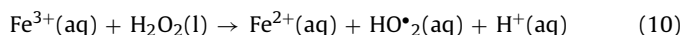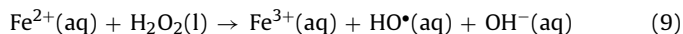
The pH of the solution is an important operating factor influencing the performance of the EC process, and the effect of current density on the pH variation during electrolysis can be a drawback. High current densities promote the formation of hydroxyl ions due to the water reduction, which depends on the amount of electricity passing through the solution [29]. Under certain conditions, various complex and polymer compounds can be formed via hydrolysis and polymerization reaction of the electrochemically dissolved metal ions [19]. The influence of pH in the EC efficiency treatment of leachates was also subject of study by some authors [20,23,26–28]. Organic load removal at different initial pH values, ranging between 3 and 10, was assessed for landfill leachates with different characteristics. It was observed that higher COD removal efficiencies were obtained at neutral conditions, whereas in acidic or alkaline medium COD removal was found to decrease [20,28]. According to literature, at pH 5.5–8.5, the majority of electrogenerated Fe^{3+} forms Fe(OH)$_3$ flocs that can remove rapidly the pollutants molecules by complexation or electrostatic attraction, followed by coagulation [9]. In contrast, at pH < 3.0 soluble Fe^{3+} is the dominant species and Fe(OH)$_3$ flocs are quite poorly produced, whereas at pH > 9.0 a part of Fe(OH)$_3$ is solubilized as Fe(OH)$_4$$^-$ and lower amount of pollutants can be separated [9]. When aluminum electrodes are used, in the pH range of 4–9, Al(OH)$^{2+}$, Al(OH)$_2$$^+$, Al$_2(OH)_2$$^{4+}$, Al(OH)$_3$ and Al$_{13}$(OH)$_{32}$$^{7+}$ are formed [19]. The surface of these compounds has large amounts of positive charge, which can lead to adsorption electrochemistry neutralization and net catching reaction. At pH > 10, Al(OH)$_4$$^-$ is dominant, and the coagulation effect rapidly decreases. At low pH, Al^{3+} is dominant, which has no coagulation effect [19]. pH variation along the EC treatment was also assessed [20,22,24,26–30]. An increase in the pH value was registered and was explained by the excess of hydroxyl ions produced at the cathode and, when Al electrodes are used, also by OH$^-$ release due to the occurrence of a partial exchange of OH$^-$ by Cl$^-$ in Al(OH)$_3$ [30].

Along with pH, electrical conductivity plays an important role in the electrochemical processes because, when it is low, the current efficiency decreases, and higher applied potentials are needed to avoid the passivation of the electrode, thus increasing the energy consumption. One of the most common electrolytes used to increase the conductivity is NaCl. Besides its contribution by inhibiting the electrode passivation process, described above, it also contributes to the wastewater disinfection, due to the formation of active chlorine [19]. In fact, along with the EC process, in the EC cell other electrochemical and chemical processes may occur, such as chloride oxidation to chlorine, when there are chloride ions in the solution [5]. Sanitary landfill leachates generally present high conductivity and addition of electrolyte is not needed to ensure high current efficiencies in the EC process. Despite this, Orkun and Kuleyin [28] investigated the effect of the conductivity in the EC treatment efficacy of leachates at four different conductivity values, ranging between 16.40 and 40.00 mS cm^{-1}, by using NaCl as the supporting electrolyte. These authors have found that, despite the decrease in energy consumption with the increase in conductivity, COD removal decreased steadily, maybe due to a change in the ionic strength that affects the kinetics and equilibrium of the reactions occurring between charged species during electrocoagulation. Also Li et al. [20] studied the effect of the conductivity by adding NaCl at concentrations of 819, 1500, 2000, 2500 and 3000 mg L^{-1}. It was observed that an increase in the concentration of Cl$^-$ from 819 mg L^{-1} to 2500 mg L^{-1} yield increases in COD removal from 29.8 to 38.9% and in AN removal from 23.5 to 32.6%. However, for Cl$^-$ concentration higher than 2500 mg L^{-1} no significant changes were observed. As can be seen in Table 1, the leachates used in these two studies had very different composition and so different reactions could occur during the EC process. Also, the conductivity of the raw samples used by Li et al. [20] was not presented. In fact, the different results obtained in these studies cannot be completely ascertained to conductivity since the only electrolyte used to alter this parameter was a chloride salt that, frequently, presents a unique behavior, particularly if the applied potentials are high enough to promote the formation of hypochlorite and chlorine species.
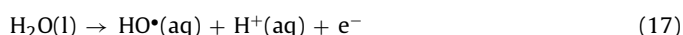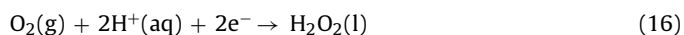
3.2. Electro-Fenton

Fenton reaction is based on an electron transfer between H_2O_2 and Fe^{2+} and was first observed by Fenton in 1984. The mixture of H_2O_2 and Fe^{2+} produces hydroxyl radicals, which are very strong oxidizing species. The classical Fenton free radical mechanism in the absence of organic compounds mainly involves the sequence of Reactions (9) to (15) [6].

$$Fe^{2+}(aq) + H_2O_2(l) \rightarrow Fe^{3+}(aq) + HO^\bullet(aq) + OH^-(aq) \quad (9)$$

$$Fe^{3+}(aq) + H_2O_2(l) \rightarrow Fe^{2+}(aq) + HO^\bullet_2(aq) + H^+(aq) \quad (10)$$

$$HO^\bullet(aq) + H_2O_2(l) \rightarrow HO^\bullet_2(aq) + H_2O(l) \quad (11)$$

$$HO^\bullet(aq) + Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + OH^-(aq) \quad (12)$$

$$Fe^{3+}(aq) + HO^\bullet_2(aq) \rightarrow Fe^{2+}(aq) + O_2H^+(aq) \quad (13)$$

$$Fe^{2+}(aq) + HO^\bullet_2(aq) + H^+(aq) \rightarrow Fe^{3+}(aq) + H_2O_2(l) \quad (14)$$

$$2HO^\bullet_2(aq) \rightarrow H_2O_2(l) + O_2(g) \quad (15)$$

Conventional Fenton process for wastewater treatment involves adding Fenton reagents (H_2O_2 and an Fe(II) salt) to the target wastewater. Besides the inconvenience of being required the addition of external H_2O_2, which is a reactive reagent and is unsafe to transport, store, and handle, the formation of Fe^{3+} during the Fenton process results in the production of iron sludge, because Fe^{3+} precipitates in the form of iron oxyhydroxides, particularly at high pH [33,34]. The resulting sludge has to be treated and disposed of properly. To overcome these drawbacks, an electro-chemical oxidation method based on Fenton reaction arose, known as the electro-Fenton process. In the EF process, the oxidation of the organic compounds occurs via an indirect electrochemical oxidation through hydroxyl radical, generated by the Fenton reaction. In this process, both species, H_2O_2 and Fe^{2+}, can be electrogenerated in situ [6].

Different configurations can be applied to operate the EF process: ferrous ion externally added and both H_2O_2 and Fe^{2+} concurrently generated at the cathode; H_2O_2 externally supplied, being a sacrificial iron anode used as ferrous ion source; H_2O_2 externally added and Fe^{2+} electrogenerated via reduction of ferric ion or ferric hydroxide sludge; or electrogenerated Fe^{2+} and H_2O_2 (via the two-electron reduction of sparged oxygen), at the sacrificial anode and at the cathode, respectively [28]. For this later case, H_2O_2 may be generated at the cathode via Eq. (16), when the cathode is made of carbonaceous materials, being O_2 directly electro-generated in the presence of noble metal anodes, as mentioned in the literature [34] (Fig. 4). During the EF process, hydroxyl radicals can be produced at the surface of a high-oxygen overvoltage anode from water oxidation, via Eq. (17) [35]. Moreover, due to continuous regeneration of Fe^{2+} at the cathode via Eq. (18), the production of hydroxyl radical would be increased (Eq. (9)) and the production of iron sludge greatly decreased [36,37].

$$O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(l) \quad (16)$$

$$H_2O(l) \rightarrow HO^\bullet(aq) + H^+(aq) + e^- \quad (17)$$

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \quad (18)$$

Nevertheless, depending on the pH of the solution, electrocoagulation can occur simultaneously with the EF process, through a mechanism in which Fe^{2+} and Fe^{3+} are converted into $Fe(OH)_n$ species and the pollutants can also be removed by electrostatic attraction and/or complexation reactions [38]. This EC process can also occur through other coagulant species besides iron-based ones, for example with aluminum species, when aluminum electrodes are used. According to the literature, the occurrence of an EC process simultaneously to
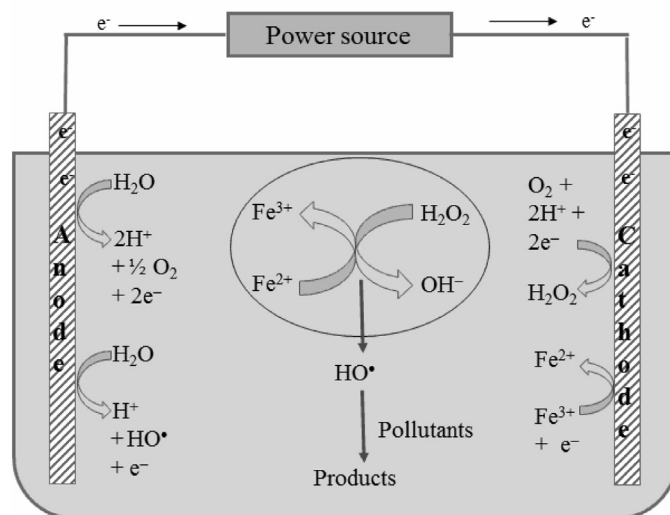

Fig. 4. Schematic diagram of an EF cell showing the main reactions involved in an EF process possessing a carbonaceous material cathode.
Source: adapted from [39].

the EF process is favored at pH range between 4.0 and 6.0 [6].

The anode and cathode materials selection is one of the key steps in the EF process. For instance, the selection of an unstable anode material will cause deterioration of the electrode in the electrolytic cells, and a high-oxygen overvoltage anode can produce hydroxyl radicals in the EF process [39]. Pt is one of the most used anode material in the EF process due to its good conductivity and chemical stability even at high potentials and in very corrosive media, but it is very expensive [39]. Regarding the cathode material, there are several materials being used, namely, carbon felt, carbon-polytetrafluoroethylene (carbon-PTFE), stainless steel, among others.

The EF process has been applied for sanitary landfill leachate treatment and there are several reports describing these experiments. Table 2 presents a compilation of these reports, with a brief summary of the main experimented conditions and the COD or total organic carbon (TOC) removals obtained. Configurations where hydrogen peroxide was externally dosed were applied for most of the EF studies with landfill leachates. This is due to the fact that, when hydrogen peroxide is generated in situ, a longer treatment time is required for high strength wastewater, such as landfill leachate [37]. Despite this, Wang et al. [34] decided to explore the main advantage of the EF technology, i.e., in situ H_2O_2 generation, using a carbon-PTFE cathode with oxygen feeding into the electro-Fenton system, applied to the treatment of landfill leachate concentrates generated from nanofiltration of biologically pretreated landfill leachate, and containing high concentrations of refractory organic compounds and inorganic salts. Experiments were conducted using 200 mL of the leachate concentrate with a carbon-PTFE electrode area of 10 or 20 cm^2, and the results have shown that carbon-PTFE cathode had a strong reactivity to produce enough H_2O_2 in situ [34].

In the studies presented in Table 2, different anode and cathode materials can be found, related to the type of configuration applied. The most used materials are Fe, Al and Pt for the anode, and Fe, Al and carbon for the cathode.

Among the several operational parameters that affect the effectiveness of the EF process, Fenton reagents concentration is one of the major factors that limit the performance of the process. Excess or shortage of the Fenton reagents, H_2O_2 or Fe(II), results in the occurrence of scavenging reactions through Eqs. (11) and (12)

Table 2
A summary of research results previously reported for the degradation of sanitary landfill leachates by electro-Fenton.

Anode/cathode	Inter-electrode gap/cm	COD_0/mg L^{-1}	$[H_2O_2]$/mg L^{-1}	$[Fe^{2+}]$/mg L^{-1}	$[H_2O_2]/[Fe^{2+}]$	pH_0	Applied current intensity/density	Operation time/min	COD or TOC removal/%	References
Fe/Fe	0.9	11000	250	NS	NS	3.4	200 A m^{-2}	30	COD: 35[a]	[28]
			5000						COD: 66	
			10000						COD: 66[a]	
Fe/Fe	1.5	951	500	NS	NS	4	2.5 A	16	COD: 66	[41]
			1000					31	COD: 70	
			1250					39	COD: 70	
		1940	NS			2	NS	30	COD: 48[a]	
						4			COD: 70[a]	
						7			COD: 46[a]	
Fe/Fe	NS	2350	250	NS	NS	3	2 A	20	COD: 32[a]	[38]
			1000						COD: 50[a]	
			2000			2	1 A	30	COD: 14[a]	
						3		20	COD: 56[a]	
								30	COD: 64[a]	
							2 A	20	COD: 72[a]	
							3 A		COD: 72[a]	
	1						2 A	NS	COD: 67[a]	
	1.8								COD: 75[a]	
	2.8								COD: 79[a]	
	4								COD: 63[a]	
	NS					4	1 A	30	COD: 46[a]	
			2500			3	2 A	20	COD: 72[a]	
Al/Al	3	2950	NS	NS	0.2	3.5	500 A m^{-2}	30	COD: 65	[43]
					1	2			COD: 80	
						3	490 A m^{-2}	43	COD: 94	
						3.5	200 A m^{-2}	30	COD: 75	
							500 A m^{-2}		COD: 88	
							800 A m^{-2}		COD: 85	
						5	500 A m^{-2}		COD: 63	
					1.8	3.5			COD: 79	
Al/Al	3	350[a]	1700	2800	1	3	490 A m^{-2}	43	COD: 96	[47]
		1500[a]							COD: 93	
Ti/RuO$_2$−IrO$_2$/NS	2.1	5000	2720[a]	373[a]	12	3	2 A	75	COD: 70[a]	[35]
			11560[a]	0	0				COD: 65	
	0.7			1568[a]	12				COD: 74	
	1.3								COD: 80	
	2.1						1 A		COD: 43[a]	
							2 A		COD: 81	
							2.5 A		COD: 87	
							3 A		COD: 79	
	2.8						2 A		COD: 72	
	2.1			2128[a]	9[a]				COD: 83	
				6720[a]	3[a]				COD: 76[a]	
				2007[a]	12				COD: 81[a]	

Ti/RuO$_2$–IrO$_2$–SnO$_2$–TiO$_2$/Ti	2	2720	2890^a	793^a	6	3	1 A	120	COD: 46	[37]
			5780^a	3173^a	3				COD: 65^a	
				1587^a	6				COD: 62	
	1			1058^a	9				COD: 55	
	2								COD: 58	
	3								COD: 56	
	2						5			COD: 55
							8			COD: 17
			8670^a	2380^a	6	3			COD: 60	
Ti/RuO$_2$–IrO$_2$/stainless steel	1.5	1500	680^a	90^a	12.5	4	2.5 A	70	COD: 47^a	[42]
			3060^a	252^a	20^a				COD: 50^a	
				403^a	12.5^a		0.5 A		COD: 50^a	
						2	2.5 A		COD: 51^a	
						3			COD: 52^a	
						4			COD: 69^a	
						6			COD: 53^a	
						4	4.5 A		COD: 60^a	
				1008^a	5^a		2.5 A		COD: 52^a	
			4760^a	627^a	12.5^a				COD: 69^a	
Pt/Carbon-PTFE	NS	3896	NS	0	NS	3	300 A m^{-2}	365	TOC: 42	[34]
				560^a			100 A m^{-2}		TOC: 55^a	
						2	300 A m^{-2}		TOC: 60^a	
						3			TOC: 74	
						5			TOC: 71^a	
						3	400 A m^{-2}		TOC: 72^a	
				2240^a		3	300 A m^{-2}		TOC: 70^a	
Pt/Carbon	NS	10200	NS	NS	NS	3	0.3 A	420	COD: 41	[46]
							1 A		COD: 61	
								480	COD: 78	

NS–Not specified.

^{a} Value obtained indirectly from data presented in the paper or from a figure.

[40]. The effect of the Fenton reagents concentration on the performance of EF process applied to landfill leachates was studied by several authors [28,34,35,37,38,41–43]. Higher H_2O_2 dosages generally results in increased COD removals, although the effectiveness of H_2O_2 is decreased when its dosage is increased beyond a certain point. In fact, hydrogen peroxide is the main source of hydroxyl radicals in electro-Fenton process (Eq. (9)) and low H_2O_2 concentrations will not generate enough hydroxyl radicals to achieve relatively high COD removals. On the other hand, if H_2O_2 concentration is too high, a decrease in COD removal can happen due to the hydroxyl radical scavenging effect of H_2O_2 (Eqs. (11) and (19)) that can result in iron sludge flotation or decreased sludge sedimentation, because of the O_2 off-gassing, and due to the recombination of the hydroxyl radicals (Eq. (20)) [33,39]. Another explanation for the decrease in H_2O_2 effectiveness when its dosage is increased beyond a certain point could be the formation of short chain organic acids which are difficult to be further oxidized [33,42].

$$HO^{\bullet}_2(aq) + HO^{\bullet}(aq) \rightarrow H_2O(l) + O_2(g) \qquad (19)$$

$$2HO^{\bullet}(aq) \rightarrow H_2O_2(l) \qquad (20)$$

Regarding the ferrous ion concentration effect, experiments showed that the addition of Fe^{2+} greatly improved organic load removal, which increased rapidly when Fe^{2+} concentration increased [34,35,37,42]. This was expected, since the concentration in hydroxyl radical, the main oxidizing agent in the EF process, increases with the increase in Fe^{2+} concentration (Eq. (9)). Using a Fe^{2+} concentration of $2128\,mg\,L^{-1}$, a COD removal of 83% was attained, and at a Fe^{2+} concentration of $560\,mg\,L^{-1}$, a TOC removal of 74% was achieved [34,35]. However, the same authors found that further increase in Fe^{2+} concentration led to a decrease in COD removal. A plausible explanation for this behavior could be the consumption of hydroxyl radicals caused by the excess of ferrous ions through a competitive reaction between hydroxyl radicals and ferrous ions, which could diminish the concentration of hydroxyl radicals as in Eq. (12) [39,42]. Wang et al. [34] believe that this decrease was mainly because more $Fe(OH)_3$ precipitates on the cathode at higher $FeSO_4$ dosages, which decreased the active sites on the cathode for producing H_2O_2. According to the authors, these results indicated that there is an optimum $[H_2O_2]/[Fe^{2+}]$ ratio for COD removal. Low $[H_2O_2]/[Fe^{2+}]$ ratio would lead to a faster disappearance rate of ferrous ion as well as hydroxyl radical via Eq. (12). On the other hand, high $[H_2O_2]/[Fe^{2+}]$ ratio would enhance the reaction between H_2O_2 and hydroxyl radical, through Eq. (11), and lead to the production of hydroperoxyl radical, a species with much weaker oxidizing power when compared to hydroxyl radical. Therefore, there is an optimum $[H_2O_2]/[Fe^{2+}]$ ratio so that the consumption of hydroxyl radical by Fe^{2+} or H_2O_2 would be minimal via Eqs. (11) or (12) [35]. However, the optimum $[H_2O_2]/[Fe^{2+}]$ ratio presented in the literature for landfill leachates is little consensus, since values between 1 and 12 can be found [35,37,42,43]. This dissimilarity is attributed to the type of pollutants present, to the matrix effect in landfill leachates and to the various methods for determining the optimum dosage [6,33].

Hydrogen peroxide feeding mode also affects EF process. The addition of H_2O_2 at beginning or during the reaction imply changes in the $[H_2O_2]/[COD]$ and $[H_2O_2]/[Fe^{2+}]$ ratios and, consequently, in the COD removal [44]. Zhang et al. [45] showed that the efficacy of the Fenton process for the treatment of landfill leachate was improved by adding H_2O_2 in multiple steps when compared with the addition in a single step. In a later study, where EF method was applied to landfill leachate treatment using a electrolytic batch reactor containing 200 mL solution, Zhang et al. [35] experienced to add H_2O_2 in a single step (at 0 min), in two steps (at 0 and 30 min), in three steps (at 0, 15 and 30 min), in four steps (at 0, 10, 20 and 30 min) or in continuous mode for 30 min. The results showed that

COD removal increased with the fractioning of dosage and the highest removal (79%) was achieved when continuous addition mode was used. According to the authors, the single step addition of H_2O_2 at the beginning of the experiments results in a rapid and efficient production of hydroxyl radicals, and parasite reactions of hydroxyl radicals with H_2O_2 (Eq. (11)) as well as ferrous ion (Eq. (12)) become predominant. Stepwise addition keeps the H_2O_2 concentration at relatively low levels, reducing the detrimental effect of hydroxyl radical scavenging (Eq. (11)) to the maximum extent, explaining why the highest COD removal was achieved when continuous addition mode of H_2O_2 was employed [35].

Due to the well-known influence of pH on iron speciation and on H_2O_2 decomposition, this parameter has been widely studied in landfill leachate treatment by the EF process [45]. pH values used in the different studies are shown in Table 2 and it can be seen that the most studied pH range varied between 3 and 4, although pH values between 2 and 8 have been tested. Wang et al. [34] investigated the effect of the initial pH on TOC removal by varying initial pH between 2 and 5. An optimum pH value of 3 was determined by these authors, which is in agreement with other studies [37,38,43], although Lin and Chang [41] and Zhang et al. [42] found maximum removal at pH of 4 (Table 2). At pH values different from the optimum (lower or higher), a decrease in the organic load removal was observed. According to literature, at high pH values (especially pH > 5) some events can occur that inhibit organic load removal, namely: (i) production of CO_3^{2-} and HCO_3^- with consequential scavenging of hydroxyl radicals, (ii) decrease in the oxidation potential of the hydroxyl radicals, (iii) deactivation of Fe^{2+} by formation of ferric hydroxides, (iv) decrease in hydroxyl radical production by the absence of H^+ and (v) decomposition of H_2O_2 to water and oxygen [6,33,39]. At low pH values (particularly at pH < 3) organic matter oxidation is also inhibited. Iron species form stable complexes with H_2O_2 leading to the deactivation of Fe^{2+} [39]. At extremely low pH values, the formed $[Fe(H_2O)]^{2+}$ reacts relatively slowly with H_2O_2, producing less hydroxyl radicals [6]. Also, the electro-generated H_2O_2 will react with H^+ to form $H_3O_2^+$ that will decrease the reaction rate between H_2O_2 and Fe^{2+} (Eq. (9)) and, consequently, less hydroxyl radicals will be produced [34].

Another important operational parameter in the EF process is the applied current intensity. An increase in the applied current predictably would lead to an increase in the electro-regeneration of Fe^{2+} from Fe^{3+} (Eq. (18)), which in turn would increase the Fenton chain reactions efficacy [35]. However, under high applied currents, competitive electrode reactions, such as oxygen discharge at the anode (Eq. (21)) and hydrogen evolution at the cathode (Eq. (22)), would increase and would inhibit the main reactions (Eqs. (17) and (18)) [35]. In sum, the use of a high applied current intensity would greatly increase the energy consumption of the process without meaning a considerable improvement in the treatment efficacy [38]. Thus, the amount of current applied to the electrodes must be determined carefully to avoid additional energy consumption.

$$2H_2O_2(l) \rightarrow 4H^+(aq) + 2O_2(g) + 4e^- \qquad (21)$$

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad (22)$$
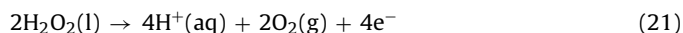
The effect of the electrical current on the organic load removal from landfill leachates by EF was studied by several authors (Table 2) [34,35,38,42,43,46]. The obtained results showed that, despite the increase with applied current in the organic load removal, measured as COD or TOC, it steadies or starts decreasing when further increases in current are applied. Optimum current densities between 300 and $500\,A\,m^{-2}$ were reported for most of the electro-Fenton studies performed with landfill leachates.

The distance between the electrodes also affects pollutants removal in the EF process. According to Eq. (18), Fe^{2+} would be regenerated via the reduction of ferric ion at the cathode, induc-

ing Fenton chain reactions. If electrodes are placed too near, the electro-regenerated Fe^{2+} could be easily oxidized to ferric ion at the anode, which would inhibit Fenton chain reactions [35]. On the other hand, the decrease in the distance between the electrodes would lead to a decrease in the ohmic drop through the electrolyte and to an equivalent decrease of the cell voltage and of the energy consumption. Large inter-electrode distance affects the limiting mass transfer of ferric ion to the cathode surface that governs ferrous ion regeneration [35]. An optimum distance range must be settled to maximize COD removal. Zhang et al. [35] reported identical COD removals for electrodes distance between 1.3 and 2.1 cm and a decrease in that removal for shorter or larger distances. Alike results were found by Atmaca [38] using an EF batch reactor with 4 monopolar electrodes in parallel connections and a leachate volume of 0.5 L, which reported a 10% increment in COD removal when inter-electrode distance was between 1.8 cm and 2.8 cm and lower removals for shorter or larger distances. According to this author, increasing the distance between the electrodes significantly raises the energy costs of the EF process and, therefore, the minimum distance between the electrodes should be selected. More recently, Zhang et al. [37] studied the influence of the inter-electrode gap in the electro-Fenton process operated at continuous mode, with two anodes and three cathodes positioned alternately, using a leachate volume of 0.8 L, and found that this influence was not so pronounced as in batch mode. COD removals were 55, 58 and 56%, respectively, when inter-electrode gaps were 1, 2 and 3 cm. According to the data presented in Table 2, a range between 1.5 and 3 cm can be considered as the most suitable range for maximum COD removal from sanitary landfill leachates.

Although initial COD is not a critical operational parameter in the EF process, its effect on COD removal was studied by Zhang et al. [35]. Higher COD removal rates were reported at higher COD initial values. Authors attained COD removals of 89, 88, 71 and 68% when initial COD was 1000, 2000, 3000 and 4000 mg L^{-1}, respectively, but the absolute COD removals were 892, 1675, 2136, and 2726 mg L^{-1}, respectively, meaning that, although the percentage removal is higher when initial COD is low, the amount of COD removed is higher at higher initial COD values. A more recent study by Aziz et al. [47] also reveals higher COD removals (absolute value) at higher COD initial values. Authors reported that for initial COD of 350 and 1500 mg L^{-1} (medium values), removals of 336 and 1395 mg L^{-1} were obtained, respectively. In fact, EF process revealed to be an effective alternative for sanitary landfill leachates treatment. COD removals above 65% were attained in all studies reported with this kind of wastewater. Operating parameters optimization was investigated using response surface methodology (RSM), Doehlert matrix, and computational fluid dynamics (CFD) [43,46,48]. Mohajeri et al. [43] reported that for the optimum conditions found, [H_2O_2]/[Fe^{2+}] ratio of 1, applied current density of 49 mA cm^{-2}, pH 3, and operation time of 43 min, for a landfill leachate with an initial COD of 2950 mg L^{-1}, COD and color removals of 94% and 96% were achieved, respectively. In the study performed by Trabelsi et al. [46], a carbon felt piece of 132 cm^2, placed in the inner wall of the cell, covering the totality of the internal perimeter, was used as working electrode and a platinum grid (4.5 × 3.1 cm), placed in the center of the cell, was used as the counter electrode. At the optimum conditions determined, i.e., applied current intensity of 1 A, pH 3 and operation time of 8 h, they yielded 78% of COD removal, being the residual COD composed by non-toxic and biodegradable short-chain carboxylic acids [46]. Optimum conditions for the maximum COD removal (92%) were found by Davarnejad et al. [48] at [H_2O_2]/[Fe^{2+}] ratio of 1.16, current density of 59.29 mA cm^{-2}, pH 3.27 and operation time of 41.7 min.

The performance of EF process in removing coliforms from landfill leachate was also investigated [47]. The method successfully removed a high percentage of coliforms from different leachate
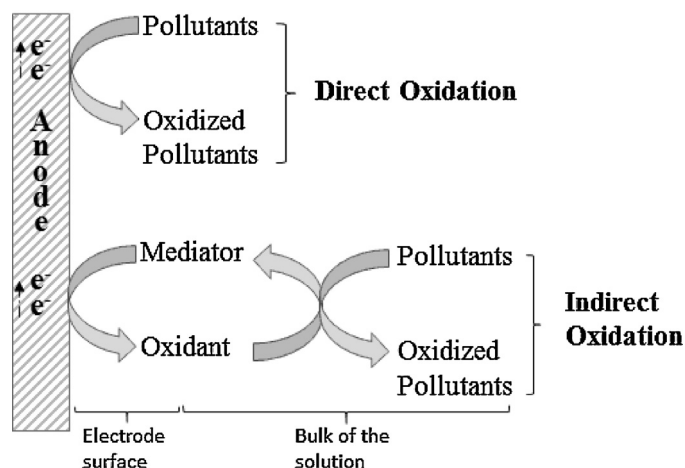

Fig. 5. Schematic depiction of the direct and indirect mediated oxidation mechanisms in the AO processes.
Source: adapted from [7].

samples, from two landfill sites with different characteristics and different coliforms concentrations.

3.3. Electrochemical oxidation

Electrochemical oxidation is the most popular electrochemical procedure for removing organic pollutants from wastewaters [9]. It is a process based on the effluent electrolysis and, in its simplest form, consists in the oxidation of pollutants in an electrolytic cell, which is formed by two electrodes connected by an external circuit, so that electrochemical reactions can take place. The electrochemical oxidation of organic pollutants can be performed by direct and indirect oxidation (Fig. 5) [9,49]. The direct oxidation, where pollutants exchange electrons directly with the anode surface, is not very effective in the degradation of organics mainly because of the electrode deactivation due to the formation of a polymeric layer in the anode surface. However, direct oxidation can promote the formation of powerful oxidations agents used in indirect oxidation processes. The indirect oxidation may occur on the electrode surface by mediation of hydroxyl radicals continuously formed during water discharge and/or on the bulk of the solution by other powerful electrogenerated oxidants, such as active chlorine, persulfate, etc.

Depending on the anode material, the hydroxyl radicals mediation can promote the partial oxidation and selective oxidation of the organic pollutant and also its complete mineralization. To interpret this behavior, Comninellis [50] has proposed a model for the organic compounds oxidation with hydroxyl radicals considering the existence of two types of anodes, the "active" and the "non-active" ones. Some examples of "active" anodes are Pt, IrO_2 and RuO_2. On the other hand, PbO_2, SnO_2 and boron-doped diamond (BDD) are examples of the "non-active" anodes. A "non-active" electrode does not provide any catalytic active site for the adsorption of reactants and/or products from the aqueous medium. In this case, the anode serves only as an inert substrate, which can act as a sink for the removal of electrons [9].

Although the model proposed by Comninellis [50] assumes that EO is mediated by hydroxyl radicals, either adsorbed at the surface, in the case of "active" anodes, or very weakly adsorbed, in the case of the "non-active" ones, as mentioned before, there are other oxidizing species that can also be generated by oxidation at the anode, such as ozone, generated from water discharge at the anode, H_2O_2, and Cl_2, HClO and ClO$^-$, derivate from Cl$^-$ oxidation at the anode, and peroxodisulphate, peroxodicarbonate and peroxodiphosphate,

from the anodic oxidation of bisulfate (or sulfate), bicarbonate and phosphate, respectively [9,12].

During the electrochemical oxidation of an aqueous effluent, the oxidation mechanisms may follow two different routes: (i) electrochemical conversion, in which organic compounds are partially oxidized and transformed into a more biodegradable reaction by-products, being a subsequent treatment still required, generally a biological one and (ii) electrochemical combustion, where organic compounds are completely mineralized and transformed into water, carbon dioxide and other inorganic species, being no further purification required [6,8,12]. The nature of the anode material also strongly influences the selectivity and the efficacy of the EO process [9]. Thus, its choice must be well considered. Competition between the oxidation of organic compounds at the anode and the oxygen evolution side reaction must be taken into account and can be analyzed by the oxygen evolution overpotential of the anodes' material. Anodes with low O_2 overvoltage will present high electrochemical activity toward oxygen evolution and low chemical reactivity toward organic compounds oxidation. Due to the production of oxygen, a significant decrease in current efficiency is expected at high current densities, which means that effective oxidation of pollutants at these anodes may occur at low current densities. On the other hand, at high O_2 overvoltage anodes, higher current densities may be applied with minimal contribution from the oxygen evolution side reaction and thus these anodes are usually chosen for the EO process [9]. Among the most commonly used anodes in EO, BDD electrodes have been reported to yield the highest organic oxidation rates and the greatest current efficiencies [8]. In fact, this anode material presents extraordinary properties such as an inert surface with low adsorption properties, remarkable corrosion stability even in strongly acidic media and extremely high O_2 evolution overvoltage [49,51].

A theoretical model to predict COD decay and instantaneous current efficiency (ICE), during the electrochemical oxidation of organic pollutants on BDD electrodes in a batch recirculation system under galvanostatic conditions, was developed by Panizza et al. [52]. The model assumes that the rate of the electrochemical mineralization of the organic compounds, with electrogenerated OH radicals and/or direct electron transfer, is a fast reaction and it is controlled by mass transport of the organic compounds toward the anode. Depending on the applied current density, two different operating regimes are identified: electrolysis under current control and electrolysis under mass transport control. Despite this model [52] has shown excellent agreement with experimental results obtained in the electrooxidation by BDD anodes of synthetic solutions of single organic compounds, it has also shown deviations when dealing with complex mixtures such as those found in landfill leachates, where the presence of electrogenerated secondary oxidants also contributes to the overall kinetics [8].

Application of the EO process to sanitary landfill leachates treatment has been reported by numerous authors. A summary of the studies performed and of the main experimental conditions tested, as well as the respective results, is presented in Table 3. As it can be seen there, several anode materials have been investigated for EO of sanitary landfill leachates, being BDD the most studied, followed by Ti/PbO$_2$, Ti/RuO$_2$-IrO$_2$ and graphite, among others. Chiang et al. [53] applied four different anode materials, with a geometric surface area of 40 dm^2, to treat a sanitary landfill leachate with a BOD/COD ratio of 0.2: graphite, Ti/PbO$_2$, binary oxide-coated titanium Ru–Ti oxide (DSA) and ternary Sn–Pd–Ru oxide coated titanium (SPR), and found that the best results for COD and ammonium removals were obtained in the following order SPR > DSA > Ti/PbO$_2$ > graphite. Also, these authors found that chlorine/hypochlorite production efficiencies of these four anode materials followed that same order, indicating that indirect oxidation by chlorine/hypochlorite could be dominant in landfill leachates EO. The high removals obtained with

SPR anode were attributed to the high current efficiency owned to its high electrocatalytic activity and high O_2 evolution overvoltage [53]. Cossu et al. [54] reported that no significant differences on COD and ammonium removals were found between Ti/PbO$_2$ and Ti/SnO$_2$ anodes. According to these authors, this happens because both materials have close oxygen evolution overpotentials. A comparison between Ti/Pt, PbO$_2$ and graphite anodes, with an active surface of 0.6 dm^2, applied to sanitary landfill leachates EO, showed that Ti/Pt anode allowed the highest COD, ammonium and color removals [55]. More recently, studies comparing BDD and metallic oxides anodes were performed [56,57]. When BDD was compared with TiRuSnO$_2$ and PbO$_2$ [56], using an undivided electrolytic flow cell under galvanostatic conditions, where electrodes had a geometric area of 50 cm^2 and an interelectrode gap of 0.5 cm, results showed that whereas BDD yields complete COD, color and ammonium removal, with PbO$_2$ a residual COD (115 mg dm^{-3}) remained and, when TiRuSnO$_2$ was used, the organic pollutants were only partially oxidized, obtaining reductions of COD, color and ammonium of 35%, 52% and 65%, respectively. Also, faster oxidation rate, higher current efficiency and lower specific energy consumption were achieved using the BDD anode, consequently, resulting in lower treatment costs [56]. Different results were achieved when Ti/Pt/PbO$_2$ and Ti/Pt/SnO$_2$–Sb$_2$O$_4$ anodes were used, with an area of 10 cm^2 and a gap between anode and cathode of 2.0 cm [57]. In fact, these anode materials presented COD removals similar to BDD and lower energy consumptions, although the difference between the COD and dissolved organic carbon (DOC) removals for BDD was less pronounced than for the other anodes, suggesting that BDD promotes more easily the complete combustion of the organic matter. According to the authors, this is due to the inert surface of BDD anodes and the consequent weak adsorption of hydroxyl radicals, which make them very reactive toward the complete oxidation of the organic compounds. Alternatively, for Ti/Pt/PbO$_2$ and Ti/Pt/SnO$_2$–Sb$_2$O$_4$, hydroxyl radicals are expected to be more strongly adsorbed on the surface; consequently, they promote the conversion of the organic matter into highly oxidized by-products rather than resulting in mineralization. Regarding nitrogen removal, metal oxide anodes were found to be more effective in the ammonium removal, whereas BDD was more efficient in the organic nitrogen removal, which was in agreement with the theory previously presented that hydroxyl radicals are weakly adsorbed on BDD and, consequently, they are more efficient in the oxidation of larger molecules with lower diffusion coefficients than metal oxides, which are more effective in the oxidation of smaller molecules with higher diffusion coefficients, because their oxidation occurs at the electrode surface where the hydroxyl radicals are more strongly adsorbed [57]. From Table 3, it can be seen that BDD anodes were the most used in EO studies with sanitary landfill leachates. In a general way, the best results for the EO of the sanitary landfill leachates were attained using BDD anodes, having been reached removals of 100% in COD and ammonium contents, although other anode materials presented very promising results.

EO experiments with landfill leachates have been conducted either at laboratory and pilot plant scale [58–60]. Undivided cells with two-dimensional static parallel or cylindrical electrodes are generally used, operating in batch mode, with or without recirculation or with stirring. Alternatively, a three-dimensional electrode electrochemical reactor has been chosen by Zhang et al. [61] to provide larger electrode surface and higher mass transfer. Performances of electrochemical reactors with two- and three-dimensional electrodes were compared and results showed that, despite no significant differences were found in the COD removal, AN removal was higher in the electrochemical reactor with a three-dimensional. COD removals of 20.2 and 26.5% and AN removals of 57.7 and 81.1% were achieved with two- and three-dimensional electrodes, respectively, under identical experimental conditions.

Table 3
A summary of research results previously reported for the degradation of sanitary landfill leachates by electrochemical oxidation.

Anode material	Applied intensity or current density	Volume treated/L	Flow rate/L h⁻¹	Electrolysis time/h	COD_0/mg L⁻¹	AN_0 /mg L⁻¹	$[Cl^-]_0$/mg L⁻¹	COD removal/%	AN removal/%	Energy consumption	References
Graphite Ti/PbO₂	750 A m⁻²	0.6	NA	4	4550[a]	2550[a]	2500	21	11	NS	[53]
								27	33		
							5000	34[a]	44[a]		
DSA							2500	29	36		
SPR	500 A m⁻²						5000	27[a]	38[a]		
	750 A m⁻²						2500	30	38		
							5000	35[a]	57[a]		
	1500 A m⁻²							38[a]	80[a]		
							10000	92	100[a]		
Ti/PbO₂ Ti/SnO₂	20 to 400 A m⁻²	0.3	1.1 to 5.4	NS	1200	380	1600 3600	up to 87.5	up to 100	NS	[54]
Pt/Ti	100 A	5	2400	2.5	53300	1094	3500	84[a]	100	40 W h (g COD)⁻¹[a]	[73]
Ti/TiO₂–RuO₂	480 A m⁻² 1160 A m⁻²	13.5	2000	3	1790 1855	1380 1060	2560 2800	33 73	NS 49	NS	[62]
BDD	150 A m⁻² 300 A m⁻²	1	660	8 4	773 1030[a]	487 742[a]	1900 1420 3670 8570	100 88[a] 86[a] 86[a]	100 35[a] 70[a] 95[a]	NS	[69,70]
	900 A m⁻²			6	3800	1710	2760	100	100		
BDD	300 A m⁻² 600 A m⁻² 1200 A m⁻²	230	18000	4	1000	783	1640	60[a] 82[a] 100[a]	25[a] 50[a] 85[a]	NS	[58]
Graphite carbon	400 A m⁻² 600 A m⁻² 800 A m⁻²	0.5	NA	4	1870 500 1185 1870	NS	NS	38 57 65 66 70	NS	NS	[63]
Ti/Pt	50 A m⁻² 150 A m⁻² 400 A m⁻²	0.25	NA	1	2750	408	5500	23[a] 40[a] 63	NS NS 80	NS	[55]
PbO₂ Graphite								30 22	58 45		
BDD	2143 A m⁻²[a] 3000 A m⁻²[a]	10	1200	6	444	NS	NS	90[a] 90[a]	NS	NS	[84]
BDD	300 A m⁻² 1200 A m⁻²	1 250 1 250	660 18000 660 18000	NS	1370 860 1370 860	950 780 950 780	2042 1630 2042 1630	82[a]	70	60 W h (g COD)⁻¹ 50 W h (g COD)⁻¹ 155 W h (g COD)⁻¹ 160 W h (g COD)⁻¹	[59]
BDD	450 A m⁻²	1 250	660 18000	8	1100	970	1717[a]	90[a] 100[a]	93[a] 100[a]	NS 94 W h (g COD)⁻¹	[60]

Table 3 (*Continued*)

Anode material	Applied intensity or current density	Volume treated/L	Flow rate/ L h⁻¹	Electrolysis time/h	COD_0/mg L⁻¹	AN_0 /mg L⁻¹	$[Cl^-]_0$/mg L⁻¹	COD removal/%	AN removal/%	Energy consumption	References
Ti/PbO₂	0.5 A 2 A 3 A	0.35	420 50 420	4 NS 4	780	NS	1800	42[a] 65[a] 68[a] 80 81[a]	NS	NS 90 kW h m⁻³ NS	[64]
Ti/RuO₂–IrO₂	300 A m⁻² 900 A m⁻²	0.8	NA	NS	3782	3143	3702	20 10	35 85	NS	[61]
BDD	1200 A m⁻²[a] 1714 A m⁻²[a] 2571 A m⁻²[a]	10	600	8	3385	1235	2574	30[a] 35[a] 50[a]	19[a] 21[a] 30[a]	98 kW h m⁻³ 190 kW h m⁻³ 360 kW h m⁻³	[68]
Ti/IrO₂–RuO₂	80 A m⁻² 160 A m⁻² 320 A m⁻²	0.12	NA	4	2960	14	6150 9695[a]	20[a] 40[a] 35[a] 75[a]	NS	NS NS 79 W h (g COD)⁻¹ 20 W h (g COD)⁻¹	[71]
Ti/RuO₂–IrO₂	260 A m⁻² 680 A m⁻²	0.2	NA	1.5	560	520	831	44 66	50 98	NS	[67]
BDD	50 A m⁻² 300 A m⁻² 500 A m⁻²	0.2	NA	6	5800 330 1360 5800	1210 75[a] 290[a] 1210	4400 275[a] 1100[a] 4400	8[a] 86 83 27 43[a]	NS 18 55 14 NS	NS	[65]
BDD	400 A m⁻² 600 A m⁻²	1	600	6 4 6	2863	1000	1200 5000 10000 1200	NS	60 100 100 65	NS 104 kW h m⁻³ 39 kW h m⁻³ NS	[72]
BDD	571 A m⁻²[a] 1000 A m⁻²[a] 2000 A m⁻²[a]	15 5	360	16	8900	2200	4500	15[a] 30[a] 69	NS 80	NS 90 W h (g COD)⁻¹	[66]
BDD PbO₂ TiRuSnO₂	400 A m⁻²[a]	0.35	420	2.5 4 8	780	266	1800	95 68[a] 35	100 100 65	82 kW h m⁻³ 130 kW h m⁻³[a] 150 kW h m⁻³[a]	[56]
BDD	900 A m⁻²	1	660	3	2055[a]	928[a]	2280[a]	90	NS	NS	[74]
Ti/Pt/PbO₂ Ti/Pt/SnO₂–Sb₂O₄ BDD	300 A m⁻²[a]	0.2	NA	6	6200	480	4700	37[a] 40[a] 39[a]	90 64 56	54 kW h m⁻³ 56 kW h m⁻³ 64 kW h m⁻³	[57]

NA–Not applied; NS–not specified.

[a] Value obtained indirectly from data presented in the paper or from a figure.

Batch reactors with recirculation, using parallel plate electrodes configuration, are the most applied in sanitary landfill leachates treatment by EO, probably because is the simplest configuration and the one that allows an easier access to the exchange of the cell components.

Besides the anode material and the reactor design, there are other factors that influence the efficacy of the EO process. Current density plays an important role in the E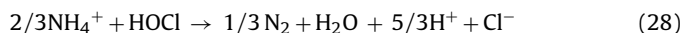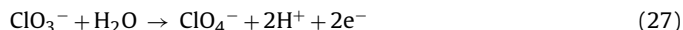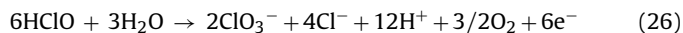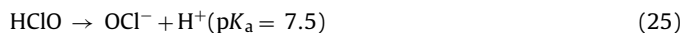O performance. In the literature revision compiled in Table 3, applied current densities ranged from 20 to 3000 A m^{-2}. Literature points to 50 A m^{-2} as the minimum current density required to achieve an effective oxidation of organics, otherwise the leachate may become darker and brown precipitates may be formed at the anode surface under weak oxidative conditions [54]. Generally, an increase in current density increases COD and AN removals. Chiang et al. [53] reported that when current density increased from 500 to 1500 A m^{-2} both COD and AN removals increased, although COD removal increased slightly, while the AN removal increased sharply. According to these authors, this increase in the removals with current density was caused by the indirect oxidation effect of chlorine/hypochlorite, which formation increased with current density. Additionally, Moraes and Bertazzoli [62] reported that color removal also strongly depends on current density, being five times higher at 1160 A m^{-2} than at 130 A m^{-2}. Similar results were described by other authors for COD and color removals [55,63–66]. In a study performed by Anglada et al. [58], it was seen that an increase in current density from 300 to 450 A m^{-2} scarcely affected the removal rate of the organic matter, but at higher current densities the oxidation levels increased with current density, which suggested a change in the oxidation mechanism of the organic matter, since at high current densities mediated electrochemical oxidation processes such as indirect oxidation by hydroxyl radicals and by electrogenerated oxidants (from the oxidation of the supporting electrolyte) had a strong influence. Also, the influence of the applied current density was much more significant in the oxidation of the ammonium than of the organic matter, even if AN removal occurred at a slower rate than that of COD. Different results were achieved by Zhang and co-workers [61,67] that reported an increase in COD removal with the increasing current density, but only until a limit of current density value is used, from which a further increase would lead to a decrease in COD removal rate. This behavior was explained by the authors taken into account that, at lower current densities, anodic oxidation of the organic matter with hydroxyl radicals was favored against chlorine evolution at the anode and thus the increase in current density would lead to the increase in COD removal. Furthermore, an increase in current density would enhance chlorine generation and hence the anodic oxidation with hydroxyl radicals would be depressed. In the meantime, the AN removal would be dominant in the competition between AN and COD removal by the indirect oxidation through chlorine/hypochlorite and, consequently, COD removal rate would decrease with current density after the highest COD removal was achieved [61,67].

Regarding energy consumption, Anglada and co-workers [59,68] found that, despite an increase in current density led to a reduction in the electrolysis time needed to reach a set out value for ammonium and COD, an higher electrical charge is involved and thus a lower efficiency. The energy consumption required to reduce the concentration of COD from an average initial value of 860 to 160 mg L^{-1}, increased from 50 kW h (kg COD)$^{-1}$ to 160 kW h (kg COD)$^{-1}$ when current density was increased from 300 A m^{-2} to 1200 A m^{-2} [59]. From the results reported above it can be inferred that an increase in current density does not necessarily results in an increase in the oxidation rate and that, for a given anode material, the effect of the current density on the treatment effectiveness depends on the characteristics of the effluent to be treated [8].

The effect of chloride ion concentration in EO efficacy of sanitary landfill leachates has also been widely studied. As can be seen on Table 3, adding extra Cl$^-$ generally improves electro-oxidation of landfill leachate, which is explained by the enhanced indirect oxidation through higher chlorine/hypochlorite production [53,54,69–72]. According to Pérez et al. [72], ammonium degradation takes place mainly due to the indirect oxidation through chlorine/hypochlorite (Eqs. (23)–(29)).

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{23}$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \tag{24}$$

$$HClO \rightarrow OCl^- + H^+ (pK_a = 7.5) \tag{25}$$

$$6HClO + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 12H^+ + 3/2O_2 + 6e^- \tag{26}$$

$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^- \tag{27}$$

$$2/3NH_4^+ + HOCl \rightarrow 1/3 N_2 + H_2O + 5/3H^+ + Cl^- \tag{28}$$

$$NH_4^+ + 4HOCl \rightarrow NO_3^- + H_2O + 6H^+ + 4Cl^- \tag{29}$$
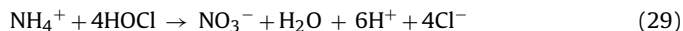
In order to clarify the indirect oxidation effect of chlorine/hypochlorite in the EO treatment of landfill leachates, Chiang et al. [53] provided additional chloride ions to the leachate as the supporting electrolyte during the electrolysis. The experimental results showed that when 2500 mg L^{-1} of additional chloride was added, both COD and AN removals increased, being the AN removal much higher than that of COD. Identical study was performed with addition of sulfate instead of chloride and a negative effect in the EO was observed, since, according to the authors, the addition of sulfate suppresses the chlorine/hypochlorite production and consequently lowers the landfill leachate treatment efficacy. Different results were found by Cossu et al. [54] with no significant variation on the COD removal by chloride addition of 1600 and 3600 mg L^{-1}, maybe due to the different current density used, 50 A m^{-2}, which is much lower than the 1500 A m^{-2} used by Chiang et al. [53].

An exceptional increase in AN removal by addition of extra Cl$^-$ was reported in different studies [69,70,72]. Pérez et al. [72] identified nitrogen and nitrate as the main products obtained from ammonium oxidation using a BDD anode and, for high chloride concentrations, nitrogen was the main product, having the percentage of ammonium converted into nitrogen increased from 74 to 85% after 4 h of treatment when the chloride content was increased from 5000 to 20,000 mg L^{-1}; regarding the conversion of ammonium into nitrate, it was observed the opposite effect, since it decreased from 26% for the chloride content of 5000 mg L^{-1} to 15% for 20,000 mg L^{-1} of chloride. Also, the formation of chloramines, chlorate and perchlorate was hindered by increasing chloride ions concentration [72]. Although high chloride concentrations generally causes a higher pollutants removal and an improvement in the landfill leachates electro-oxidation performance, the typical Cl$^-$ concentrations found in sanitary landfill leachates are not enough for effective indirect oxidation through chlorine/hypochlorite and the addition of an extra amount of Cl$^-$ is often required, which may lead to the potential formation of chlorinated organic intermediate and hazardous organic compounds as final products [7]. Regarding energy consumptions, the use of high initial chloride concentrations reduces the energy consumption (Table 3), mainly due to an increase in the conductivity, which leads to lower cell potentials [71,72].

The influence of the pH has also been studied, revealing that, when pH is increased, in the range between 6 and 9, the EO efficiency increases and, whereas at acidic pH organic and ammonium nitrogen is oxidized to nitrates, at alkaline conditions it is transformed, mainly, in nitrogen gas. Also, the formation of chloramines and the specific energy consumption decreased with the increase in pH [73].

Although the EO process is not yet fully optimized for sanitary landfill leachates treatment and there are some aspects that need further investigation and clarification, there is no doubt that EO is a technically feasible alternative to eliminate the organic pollutants from leachates. Total COD, color and ammonium removals were already reported in the EO treatment of sanitary landfill leachates [60,69,70]. Furthermore, EO process can successfully remove the existing metal ions in sanitary landfill leachates.

In a combined EC and EO sanitary landfill leachate treatment performed by Fernandes et al. [23], where EC was performed using iron consumable electrodes, with an immersed area of 40 cm^2, at an applied current intensity of 2.5 A, being the resulting effluent submitted to EO using a BDD anode, with an area of 20 cm^2, at an applied current intensity of 1 A, it was shown that chromium was almost completely removed and zinc was partially removed during EC, being the remainder of the zinc removed during EO. Also, despite iron concentration increased during EC, since consumable iron electrodes were used in the EC process, it sharply decreased during AO, by cathodic reduction. Moreover, recent studies showed that, during the EO of leachates using BDD electrodes with a surface area of 70 cm^2 at an applied current density of 900 A m^{-2}, hydroxyl radicals efficiently generated on the BDD anode surface promoted a reduction in the polychlorinated dibenzo-*p*-dioxins and dibenzo-furans (PCDD/Fs) concentrations and the samples toxicity [74].

4. Major challenges and future prospects

Efficient methods for sanitary landfill leachates remediation have been developed from electrochemical technology. Different electrode materials, cell configurations and experimental conditions have been studied. Some drawbacks were identified, being the operational costs transversal to all electrochemical methods since they are basically feed by electricity.

EC has demonstrated to be an effective and practical technology to treat leachates from sanitary landfills. Its application requires simple equipment, being easy to operate and does not require chemicals addition. Nevertheless, there are some drawbacks associated to the application of this process to sanitary landfill leachates, namely: the need for regular replacement of the "sacrificial electrodes", since they are dissolved into the wastewater streams as a result of oxidation, and the consequent increase in conductivity of the remaining effluent; the eventual formation of an impermeable oxide film on the cathode, disabling the EC unit; and, not less important, the sludge that is formed during the process, that will have in its content significant amounts of iron or aluminum and other recalcitrant pollutant species that need to be treated before its disposal. Moreover, some toxic chlorinated organic compounds and trihalomethanes may be formed in situ if chloride and high humic and fulvic acid contents are present [18].

To increase the performance of the EC process and to reduce the increase in conductivity of the remaining effluent, attention has to be paid to the metal ions concentration in solution, avoiding unnecessary high metal contents. Complementary studies to the one presented by Fernandes et al. [23] should also be performed using aluminum, to establish the ideal concentration of iron or aluminum ions in solution that allows high electrocoagulation efficiency without unnecessary waste of the sacrificial anode.

Changing the electrodes' polarity may help reducing the efficiency loss caused by the impermeable oxide film formed on the cathode. Also, constant applied intensity instead of constant applied potential decreases the electrodes' passivation, although it increases energy consumption, since, to keep the intensity when a passivating film is forming, higher overpotentials have to be applied. This increase in overpotential presents an extra feature that is the possibility of the direct oxidation of the organic matter present in the effluent. Find reliable ways of reducing

electrode's passivation and the consequent inactivation of the EC landfill leachate treatment unit can pass also by the development of different electrode types and arrangements and more sophisticated reactor operational strategies.

Integration of the EC process with other treatment methods can also be a possible solution to overcome some of the drawbacks, namely the solid–liquid separation and the sludge elimination. The EC technology can be designed to include membrane separation, reverse osmosis, electrofiltration, sludge dewatering, thermo-oxidation and other conventional technologies to enhance the recovery of fine particles and metal ions from wastewater [21]. This is an area in which urges to perform intensive work. Otherwise, EC will become just another way of transferring the problem, with the addition of metal ions to the final solution.

Integration of EC and EO processes, besides enhancing the treatment efficacy, also have the potential to eliminate possible toxic species, like chromium, zinc and part of the iron introduced during the EC process [23]. However, this study has to be further developed, to include many other metal ions that were not included in this study. Research on the best experimental conditions that will lead to a more efficient recovery of metals from solution, as well as the possibility of the selective recovery of the most dangerous metal ions or those that are present in higher concentration, are also welcome.

EF is an attractive emerging electrochemical process yielding good treatment efficiencies for landfill leachates and it is an economical technology in comparison with, for instance, conventional Fenton process [33]. However, its application to sanitary landfill leachates treatment presents some drawbacks due to the optimal pH value required for process efficiency, ranging between 3 and 4. In fact, pH of most of the sanitary landfill leachates are not within this optimal range and high amounts of chemicals are needed to acidify the effluent before its decontamination and/or to neutralize the treated solutions before disposal. Particularly in the case of leachates, pH adjustment is difficult, because this complex suspension presents a buffering effect, and huge amounts of acid may be needed to pH correction. Moreover, since EF process is feed by electricity, operational costs can also be a disadvantage of this technology. A possible solution to overcome these drawbacks is to integrate EF with other treatment technologies and such were already reported in literature for sanitary landfill leachates treatment [41,75–77]. The EF process performance in landfill leachates treatment can be improved in the presence of UV irradiation by a process called photoelectro-Fenton [78,79]. Further studies on the combination of EF process with other technologies should be conducted, so a feasible sanitary landfill leachates treatment project can be implemented. Also, as has already been done for other types of wastewaters, the application of highly active electrode materials should be explored, in order to enhance EF process efficacy and diminish the operational costs. EF process costs can also be reduced by the application of cheaper Fe^{2+} sources. The application of iron shavings, which are wastes from the iron processing industry, have already been reported in the treatment of urban landfill leachates by a Fenton-like process [80].

EO provides a simple, viable and promising method for the remediation of sanitary landfill leachates. This electrochemical method allows high treatment efficiencies without the disadvantage of sludge production. Under appropriate experimental conditions, it can remove most of the COD, almost all ammonia, and it also reduces significantly the color, without the accumulation of refractory organics.

The presence of Cl$^-$ in the leachates promotes the indirect electro-oxidation, mediated by electrogenerated active chlorine, which increases EO efficacy, but, at the same time, the production of undesirable toxic chlorinated by-products may occur, which is one of the drawbacks of the EO application to landfill leachates

treatment. Another drawback, possibly the most relevant, is the high operating costs due to the high energy consumption, since electricity is basically the only consumable in the electrochemical oxidation. To overcome this problem, there are two possible pathways: (1) the use of this technology in combination with other techniques, as a pre-treatment or a polishing step and (2) the use of renewable energy sources to power electrochemical oxidation. There are several reports describing the application of combined methods involving EO to treat sanitary landfill leachates [4,23,28,55,75,81–86]. The encouraging results obtained so far set the basis for future work. In fact, similar operating costs for conventional treatments and for EO, applied as polishing step, were already observed [84]. Regarding the use of renewable energy sources, the integration of photovoltaic modules in electrochemical wastewater treatment has been already reported [87]. Within this field, there is still a wide range of possibilities that can be explored. Development of a sustainable process based on the integration of efficient technologies is one of the key obstacles that have to be overcome before full-scale implementation of the electrochemical oxidation. Another major area for future research is the improvement of the electrocatalytic activity and electrochemical stability of new electrode materials, to develop better and more cost-effective electrodes, which will result in lower operational and capital costs.

Despite BDD electrodes exceptional properties, already described, and the good results obtained when this electrode is used, its application has been mostly studied at Si-supported devices, which present difficulties related to their industrial transposition, due to the fragility and the relatively low conductivity of the Si substrate [12]. BDD films synthesized on Nb, Ta and W are promising, but their large-scale utilization is impossible due to the unacceptably high costs of these metal substrates [12]. On the contrary, titanium would possess all required features to be a good substrate material. There are already available in literature some studies reporting the use of Ti/BDD electrodes [88–93], but its use has never been reported in EO of sanitary landfill leachates. On the other hand, lead and stannous oxides have already proved to be very efficient in the leachates treatment, and there are already lead oxide electrodes commercially available. Maybe the next important step to implement EO technology is to perform pilot scale studies, in the in-situ plants, to deal with all daily constrains and changes, to find out if the only problem associated with this technology is, in fact, the cost.

Although all the electrochemical methods treated in this paper have high potential to efficiently treat sanitary landfill leachates, before a sustainable electrochemical process can be implemented at full-scale, further research needs to be developed regarding new and/or improved electrode materials, different electrode types and arrangements and more sophisticated reactor operational strategies, in order to reduce operational costs and to overcome some other identified drawbacks. With the same goal, integration of these methods with each other or with other treatment methods should also be more explored. Outstanding works have been developed in order to switch from standard landfill management mode to a more environmentally sustainable one, and one of the latest reports have also revealed the real possibility of using blended leachate as a fertigant for the re-vegetation of the walls of the closed landfills [94].

In spite of the very good results obtained with electrochemical techniques on pollution abatement of sanitary landfill leachates, electrochemical processes are often accused of being interfacial reactions and therefore difficult or impossible to be applied to large volumes. The "interfacial problem" is, in fact, a problem shared by several unit operations already stablished at industrial level. However, it is a sort of handicap that, to be efficiently overcome, needs pilot and semi-industrial scale studies. Also, to lower the energetic costs, these technologies should be applied to partial streams or as

integrated processes with biological solutions. The energetic consumption can also be solved with green energy, like wind energy, tidal or solar, or using biogas from an anaerobic digestion reactor to produce energy to be used in the electrochemical reactor to polish the anaerobic reactor effluent. Thus, incorporating renewable energy sources in the electrochemical treatment of sanitary landfill leachates closes with a flourish future prospects in this field.

Acknowledgments

References

[1] T. Eggen, M. Moeder, A. Arukwe, Sci. Total Environ. 408 (2010) 5147–5157.
[2] C.B. Öman, C. Junestedt, Waste Manage. 28 (2008) 1876–1891.
[3] K.Y. Foo, B.H. Hameed, J. Hazard. Mater. 171 (2009) 54–60.
[4] V. Garaj-Vrhovac, V. Orescanin, G. Gajski, M. Geric, D. Ruk, R. Kollar, S.R. Brkanac, P. Cvjetko, Chemosphere 93 (2013) 939–945.
[5] G. Chen, Sep. Purif. Technol. 38 (2004) 11–41.
[6] Y. Deng, J.D. Englehardt, Water Res. 40 (2006) 3683–3694.
[7] Y. Deng, J.D. Englehardt, Waste Manage. 27 (2007) 380–388.
[8] A. Anglada, A. Urtiaga, I. Ortiz, J. Chem. Technol. Biotechnol. 84 (2009) 1747–1755.
[9] C.A. Martínez-Huitle, E. Brillas, Appl. Catal. B: Environ. 87 (2009) 105–145.
[10] I. Sirés, E. Brillas, Environ. Int. 40 (2012) 212–229.
[11] E. Brillas, P.L. Cabot, J. Casado, Chemical Degradation Methods for Wastes and Pollutants Environmental and Industrial Applications, in: M. Tarr (Ed.), Marcel Dekker, New York, 2003, pp. 235–304.
[12] C.A. Martínez-Huitle, S. Ferro, Chem. Soc. Rev. 35 (2006) 1324–1340.
[13] S. Renou, J.G. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, J. Hazard. Mater. 150 (2008) 468–493.
[14] J. Koc-Jurczyk, M. Jurczyk, The influence of waste landfills on ground and water environment, In: Contemporary Problems of Management and Environmental Protection, No. 9, Some Aspects of Environmental Impact of Waste Dumps, 2011 (Chapter 2).
[15] P. Kjeldsen, M.A. Barlaz, A.P. Rooker, A. Baun, A. Ledin, T.H. Christensen, Crit. Rev. Env. Sci. Technol. 32 (2002) 297–336.
[16] A.A. Abbas, G. Jingsong, L.Z. Ping, P.Y. Ya, W.S. Al-Rekabi, Am. J. Appl. Sci. 6 (2009) 672–684.
[17] F.N. Ahmed, C.Q. Lan, Desalination 287 (2012) 41–54.
[18] M.Y.A. Mollah, P. Morkovsky, J.A.G. Gomes, M. Kesmez, J. Parga, D.L. Cocke, J. Hazard. Mater. 114 (2004) 199–210.
[19] H. Liu, X. Zhao, J. Qu, Electrocoagulation in water treatment, in: C. Comninellis, G. Chen (Eds.), Electrochemistry for the Environment, Springer Science + Business Media, LLC, New York, 2010, pp. 245–262 (Chapter 10).
[20] X. Li, J. Song, J. Guo, Z. Wang, Q. Feng, Procedia Environ. Sci. 10 (2011) 1159–1164.
[21] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, J. Hazard. Mater. 84 (2001) 29–41.
[22] F. Ilhan, U. Kurt, O. Apaydin, M.T. Gonullu, J. Hazard. Mater. 154 (2008) 381–389.
[23] A. Fernandes, P. Spranger, A.D. Fonseca, M.J. Pacheco, L. Ciríaco, A. Lopes, Appl. Catal. B: Environ. 144 (2014) 514–520.
[24] F. Bouhezila, M. Hariti, H. Lounici, N. Mameri, Desalination 280 (2011) 347–353.
[25] J. Labanowski, V. Pallier, G. Feuillade-Cathalifau, J. Hazard. Mater. 179 (2010) 166–172.
[26] D. Norma, A. Fernandes, M.J. Pacheco, L. Ciríaco, A. Lopes, Portugaliae Electrochim. Acta 30 (2012) 221–234.
[27] D. Norma, A. Fernandes, L. Ciríaco, M.J. Pacheco, A. Lopes, Portugaliae Electrochim. Acta 30 (2012) 281–294.
[28] M.O. Orkun, A. Kuleyin, Environ. Prog. Sust. Energy 31 (2012) 59–67.
[29] C. Ricordel, H. Djelal, J. Environ. Chem. Eng. 2 (2014) 1551–1557.
[30] S. Top, E. Sekman, S. Hosver, M.S. Bilgili, Desalination 268 (2011) 158–162.
[31] S. Veli, T. Öztürk, A. Dimoglo, Sep. Purif. Technol. 61 (2008) 82–88.
[32] W.A. Pretorius, W.G. Johannes, G.G. Lampert, Water S. Afr. 17 (2) (1991) 133–138.
[33] M. Umar, H.A. Aziz, M.S. Yusoff, Waste Manage. 30 (2010) 2113–2121.
[34] Y. Wang, X. Li, L. Zhen, H. Zhang, Y. Zhang, C. Wang, J. Hazard. Mater. 229–230 (2012) 115–121.
[35] H. Zhang, D.B. Zhang, J.Y. Zhou, J. Hazard. Mater. 135 (2006) 106–111.
[36] I. Sirés, J.A. Garrido, R.M. Rodríguez, E. Brillas, N. Oturan, M.A. Oturan, Appl. Catal. B: Environ. 72 (2007) 382–394.

[37] H. Zhang, X. Ran, X. Wu, J. Hazard. Mater. 241–242 (2012) 259–266.
[38] E. Atmaca, J. Hazard. Mater. 163 (2009) 109–114.
[39] P.V. Nidheesh, R. Gandhimathi, Desalination 299 (2012) 1–15.
[40] A. Lopez, M. Pagano, A. Volpe, A. Di Pinto, Chemosphere 54 (2004) 1000–1005.
[41] S.H. Lin, C.C. Chang, Water Res. 34 (2000) 4243–4249.
[42] H. Zhang, Z.H. Cheng, D.B. Zhang, Fresenius Environ. Bull. 16 (2007) 1216–1619.
[43] S. Mohajeri, H.A. Aziz, M.H. Isa, M.A. Zahed, M.N. Adlan, J. Hazard. Mater. 176 (2010) 749–758.
[44] O. Primo, M.J. Rivero, I. Ortiz, J. Hazard. Mater. 153 (2008) 834–842.
[45] H. Zhang, H.J. Choi, C.-P. Huang, J. Hazard. Mater. 125 (2005) 166–174.
[46] S. Trabelsi, N. Oturan, N. Bellakhal, M.A. Oturan, J. Mater. Environ. Sci. 3 (2012) 426–433.
[47] H.A. Aziz, O.M. Othman, S.S. Abu Amr, Waste Manage. 33 (2013) 396–400.
[48] R. Davarnejad, M.K. Moraveji, M. Pirhadi, M. Mohammadi, Water Sci. Technol. 69 (2014) 343–349.
[49] M. Panizza, G. Cerisola, Electrochim. Acta 51 (2005) 191–199.
[50] C. Comninellis, Electrochim. Acta 39 (1994) 1857–1862.
[51] M. Fryda, D. Herrmann, L. Schäfer, C.P. Klages, A. Perret, W. Haenni, C. Comninellis, D. Gandini, New Diamond Front. Carbon Technol. 9 (1999) 229–240.
[52] M. Panizza, P.A. Michaud, G. Cerisola, C. Comninellis, J. Electroanal. Chem. 507 (2001) 206–214.
[53] L. Chiang, J. Chang, T. Wen, Wat. Res. 29 (1995) 671–678.
[54] R. Cossu, A. Polcaro, M. Lavagnolo, M. Mascia, S. Palmas, F. Renoldi, Environ. Sci. Technol. 32 (1998) 3570–3573.
[55] F. Feki, F. Aloui, M. Feki, S. Sayadi, Chemosphere 75 (2009) 256–260.
[56] M. Panizza, C.A. Martinez-Huitle, Chemosphere 90 (2013) 1455–1460.
[57] A. Fernandes, D. Santos, M.J. Pacheco, L. Ciríaco, A. Lopes, Appl. Catal. B: Environ. 148–149 (2014) 288–294.
[58] A. Anglada, A. Urtiaga, I. Ortiz, Environ. Sci. Technol. 43 (2009) 2035–2040.
[59] A. Anglada, D. Ortiz, A. Urtiaga, I. Ortiz, Water Sci. Technol. 61 (2010) 2211–2217.
[60] A. Anglada, A. Urtiaga, I. Ortiz, J. Hazard. Mater. 181 (2010) 729–735.
[61] H. Zhang, Y. Li, X. Wu, Y. Zhang, D. Zhang, Waste Manage. 30 (2010) 2096–2102.
[62] P. Moraes, R. Bertazzoli, Chemosphere 58 (2005) 41–46.
[63] M. Bashir, M. Isa, S. Kutty, Z. Awang, H. Aziz, S. Mohajeri, I. Farooqi, Waste Manage. 29 (2009) 2534–2541.
[64] M. Panizza, M. Delucchi, I. Sirés, J. Appl. Electrochem. 40 (2010) 1721–1727.
[65] A. Fernandes, M.J. Pacheco, L. Ciríaco, A. Lopes, J. Hazard. Mater. 199–200 (2012) 82–87.
[66] A. Fernandes, E. Catalão, L. Ciríaco, M.J. Pacheco, A. Lopes, J. Electrochem. Sci. Eng. 3 (2013) 125–135.
[67] H. Zhang, X. Ran, X. Wu, D. Zhang, J. Hazard. Mater. 188 (2011) 261–268.
[68] A. Anglada, A. Urtiaga, I. Ortiz, D. Mantzavinos, E. Diamadopoulos, Water Res. 45 (2011) 828–838.
[69] A. Cabeza, A. Urtiaga, I. Ortiz, Ind. Eng. Chem. Res. 46 (2007) 1439–1446.
[70] A. Cabeza, A. Urtiaga, M.J. Rivero, I. Ortiz, J. Hazard. Mater. 144 (2007) 715–719.
[71] E. Turro, A. Giannis, R. Cossu, E. Gidarakos, D. Mantzavinos, A. Katsaounis, J. Hazard. Mater. 190 (2011) 460–465.
[72] G. Pérez, J. Saiz, R. Ibañez, A. Urtiaga, I. Ortiz, Water Res. 46 (2012) 2579–2590.
[73] A. Vlyssides, P. Karlis, M. Loizidou, A. Zorpas, D. Arapoglou, Environ. Technol. 22 (2001) 1467–1476.
[74] M. Vallejo, M.F. San Román, A. Irabien, I. Ortiz, Chemosphere 90 (2013) 132–138.
[75] A. Urtiaga, A. Rueda, A. Anglada, I. Ortiz, J. Hazard. Mater. 166 (2009) 1530–1534.
[76] L. Sun, Z. Yu, Y. Chen, X. Ru, M. Li, T. Zhou, Chin. J. Environ. Eng. 7 (2013) 3972–3978.
[77] D.B. Zhang, X.G. Wu, Y.S. Wang, H. Zhang, Chem. Pap. 68 (2014) 782–787.
[78] A. Altin, Sep. Purif. Technol. 61 (2008) 391–397.
[79] H. Zhang, Y. Li, X. Wu, J. Environ. Eng. 138 (2012) 278–285.
[80] R.C. Martins, D.V. Lopes, M.J. Quina, R.M. Quinta-Ferreira, Chem. Eng. J. 192 (2012) 219–225.
[81] P. Wang, I.W.C. Lau, H.H.P. Fang, Environ. Technol. 22 (2001) 373–381.
[82] I. Ihara, K. Kanamura, E. Shimada, T. Watanabe, IEEE Trans. Appl. Supercond. 14 (2004) 1558–1560.
[83] Y. Lei, Z. Shen, R. Huang, W. Wang, Water Res. 41 (2007) 2417–2426.
[84] C. Papastavrou, D. Mantzavinos, E. Diamadopoulos, Environ. Technol. 30 (2009) 1547–1553.
[85] X. Zhao, J. Qu, H. Liu, C. Wang, S. Xiao, R. Liu, P. Liu, H. Lan, C. Hu, Bioresour. Technol. 101 (2010) 865–869.
[86] S. Xiao, J. Peng, Y. Song, D. Zhang, R. Liu, P. Zeng, Sep. Purif. Technol. 117 (2013) 24–29.
[87] E. Alvarez-Guerra, A. Dominguez-Ramos, A. Irabien, Chem. Eng. Res. Des. 89 (2011) 2679–2685.
[88] X. Chen, G. Chen, Sep. Purif. Technol. 48 (2006) 45–49.
[89] J. Sun, H. Lu, L. Du, H. Lin, H. Li, Appl. Surf. Sci. 257 (2011) 6667–6671.
[90] J. Sun, H. Lu, H. Lin, L. Du, W. Huang, H. Li, T. Cui, Sep. Purif. Technol. 88 (2012) 116–120.
[91] J. Sun, H. Lu, H. Lin, W. Huang, H. Li, J. Lu, T. Cui, Mater. Lett. 83 (2012) 112–114.
[92] J.J. Wei, Ch.M. Li, X.H. Gao, L.F. Hei, F.X. Lvun, Appl. Surf. Sci. 258 (2012) 6909–6913.
[93] Y. Juang, E. Nurhayati, C. Huang, J.R. Pan, S. Huang, Sep. Purif. Technol. 120 (2013) 289–295.
[94] G. Del Moro, E. Barca, D. Cassano, C. Di Iaconi, G. Mascolo, G. Brunetti, Environ. Sci. Pollut. Res. 21 (2014) 9366–9375.